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Introduction

The research reported in this paper was funded and supported by the Bureau of Engraving and Printing (BEP) and the National Science Foundation. The project, the title of which was "Determination of the Role of Melamine-Formaldehyde In Currency Paper" Award Number 9010053 was overseen by the Surface Engineering and Tribology Program of NSF.

The main motivation for this investigation was the removal of formaldehyde compounds from a variety of paper products, specifically currency papers.

Literature Review

Melamine-Formaldehyde (M-F) has been used since the early 1940s as a wet-strength agent. During this time attention has been focused more on the chemical rather than the physical aspects of why M-F (and other resins and wet-strength additives) functions so well as a wet-strength agent. Without a wet-strength additive, paper retains less than 10% of its dry strength when wet, while with the addition of about 3% M-F, and depending on fiber type, 40 to 50% of the dry strength can be retained. Our current understanding of the chemical and physical behavior of wet strength agents is given in the recent review by Espy[1].

With increasing moisture content and eventual saturation both inter and intra fiber bonds (primarily H-bonds) are broken. The supposed role of the wet-strength agent is to prevent or minimize the effects of these bond-breaking processes through ionic bonding (2), covalent bonding (2), and cross-linking (3), etc. Bond breaking takes place at the molecular level, however, structural failure may be precipitated by failure at a higher level of organization within the structure.

A number of theories have been proposed for predicting the elastic (4) and dry-strength behavior of paper (5), and more recently a model has been suggested for wet web strength (6). No similar models have yet been proposed for the wet-strength behavior of paper. It may be helpful to examine wet strength in terms of the variables known to control dry strength, i.e., fiber geometry, fiber strength, bond strength, relative bonded area or density. Other effects such as formation, stress concentration, etc., may also be important, but have yet to be accounted for in modelling studies.

We hypothesize that the loss in paper strength from the dry to the saturated state is due to two main effects:

1. Changes in structure primarily due to swelling

2. Changes due primarily to moisture.

This study attempts to model and measure the relative contribution of these affects to losses in wet strength.

Let us now briefly consider these effects and their impact on the variables controlling dry strength listed above.

Fiber Strength

Single fiber studies indicate that some fibers show an improvement in tensile strength when wet, whereas, others show a decrease (7). An increase in fiber tensile strength may be attributed to improved stress transfer and/or realignment of microfibrils.

Zero span measurements generally show losses in fiber strength when wet. However, the comprehensive study by Gurnagul and Page (8) demonstrates that there is no change in fiber strength in going from the dry to the wet state unless the fiber has been subjected to some level of mechanical or chemical damage to its interfibrillar matrix.

We have already noted that 45 to 50% of dry strength can be retained in the wet state. In this situation potential losses in fiber strength in the wet state are not inconsequential.

Bond Strength

We might expect that interfiber bond strength would decrease with increased moisture content. The resolution of this conjecture awaits bond strength measurements in the wet state. Regarding wet strength, the work of Craver (9) and Colson and Stratton (10) is very relevant. Stratton has found, at least for one wet-strength additive, that interfiber bond strength at 50% RH is increased with additive addition. Furthermore, he found that the mode of interfiber bond failure changed dramatically. Without a strength additive, there was a relatively clean separation of the fibers at failure; whereas, with an additive, failure occurred within the fiber cell wall. Interestingly, Craver found a similar effect in his earlier work on interfiber bond failure in the wet state. Unfortunately, he did not make any quantitative measurements of bond strength.

If wet strength agents are present it may be thought that bond strength is relatively unaffected by moisture. However, inferences from Button (11), and Stratton and Colson (12) might suggest otherwise. Moisture uptake would reduce fiber modulus, although swelling might produce favorable changes in fiber cross-sectional geometry. On the other hand, we have the fact that Craver's (9) mode of failure in the wet state is very similar to that found by Stratton in the dry state, however, this does not necessarily preclude a loss in bond strength.

Relative Bonded Area R.B.A. and Apparent Density ρ_a

With increasing moisture content, cellulose fibers swell as a result of both inter- and intrafiber bond breaking. As a consequence, the fiber network should undergo a loss in densification and

bonded area resulting in a loss of strength.

Therefore, one of the main roles of wet-strength additives may be to minimize fiber swelling (although some degree of swelling may be desirable). Other consequences of fiber swelling are an increase in fiber coarseness and possibly a deterioration in formation (mass density distribution).

In the results which follow, we attempt to separate the effects due to swelling and moisture uptake from the factors discussed above. We assume that the structural effects of swelling can be determined by measuring properties on handsheets which have been critically point dried from the wet state and then conditioned to 50% RH and 23° C. Property differences between this state and the saturated state might then be attributed to moisture effects only.

This approach has been used to try to better understand the mechanical factors controlling the wet-strength behavior of paper, and the role of M-F and other wet-strength agents.

Experimental

The furnish used in our experiments was a well-beaten blend of 70% cotton and 30% linen fibers. The nominal grammage of the handsheets was 60 g/m^2.

The wet-strength resins used were Melamine-Formaldehyde M-F and poly (amino amide) epichlorohydrin resin PAE. Following the synergistic effects of PAE and carboxymethylcellulose CMC reported by Espy (13) and Stratton (14) a blend of 70% PAE and 30% CMC was also included. The desired level of addition was 3% and we believed that resin retention would be close to 100%. However, in subsequent testing based on nitrogen-content determination M-F and PAE addition levels were closer to 2%.

In another set of experiments, the pulp was treated with chloroacetic acid ($ClCH_2COOH$) in order to increase the number of carboxyl groups and so improve the effectiveness of the wet-strength resin PAE.

Techniques to preserve the swollen state of cellulose fibers include freeze drying, solvent exchange, and critical point drying (cpd). Caulfield and Weatherwax (15) have argued that cpd is the only truly effective means of preserving the swollen state since surface tension effects are eliminated or minimized. This technique has been used for surface area measurements (15) and examination of the swollen state of cellulose fibers under the microscope (16), and preserving the swollen state of mechanical pulp fines (17).

In our procedure, samples for cpd were soaked in water for 24 hours, followed by exchange with ethanol, amyl acetate, and then CO_2, the critical properties of which are $T_c = 31.1°C$ and $P_c = 1073$ psig. The critical point drying (cpd) equipment used was Ladd Critical Point Dryer Cat. No. 28000, manufactured by Ladd Research Industries, Inc., P.O. Box 1005, Burlington,

Vermont 05402. After cpd, the samples were brought to 50% RH and 23°C for at least 24 hours prior to testing.

Unless otherwise stated, Tappi-recommended procedures were used to determine the properties measured. Non-destructive measurement of elastic properties were determined using techniques developed at IPST (formerly IPC).

Results & Discussion

The basic sheet properties are shown in Table 1. We note that the handsheets with M-F, PAE, and PAE/CMC addition have a lower density than the control. The handsheets made from chloracetic acid (ca) treated fibers have an even lower density, however, this is partly due to differences in sheet making conditions, i.e., the ca sheets were made on a British handsheet mold and the M-F handsheets were made on a Noble and Wood handsheet mold.

The conditioned strength related properties:- out-of-plane specific modulus, tensile and zero-span strength - are increased by the various wet-strength additives. Unfortunately ca treatment resulted in a large loss in fiber strength although PAE addition did produce the largest relative gain in tensile strength.

The ratio of wet weight (24-hour soak) to dry (conditioned) weight for the various conditions are given in Table 2. The predicted values of moisture pick up θ_{pred} were calculated assuming no swelling. Third column is the increase in pick up due to swelling. The untreated controls both have a greater percentage increase in pick up due to swelling.

Also shown in Table 2 is the percentage increase in caliper due to moisture pick up. The untreated control has the largest increase in caliper, while the ca treated control has a much lower increase in caliper. All of the wet-strength additives significantly reduce swelling, although in the case of the ca treated fibers, no further gain in swelling reduction is seen with the addition of PAE. The percentage retention of wet thickness achieved by cpd is shown in the last column. The retention is only fair since we expected to preserve the fully swollen state. This is an area which requires further investigation.

The apparent density of the cpd handsheets lies directly between the dry (conditioned) and wet handsheets as shown in Table 3. The loss in tensile strength of handsheets, which have been soaked for 24 hours and cpd, is quite large, but not so great as measured on the wet handsheets, particularly the controls.

Using these results and assuming a fiber density (ρ_f) of 1.55 g/cm^3, a bonding index (n) (18) has been calculated for the dry, cpd, and wet states. The results are given in Table 4. It is interesting to note that the bonding index in the cpd state is quite close, in a number of instances, to the dry (conditioned) state. However, in all cases there is a large drop in bond index values in the wet state. The bonding index values given in Table 4, i.e., n_{cpd}, have been

used to calculate values of $(T_{cpd}/T_{dry})_c$, given in Table 3. These are based on the apparent density the network should have in the wet state, i.e., the ρ_{wet} values given in Table 3.

Out-of-plane specific modulus for the dry, cpd, and wet states are given in Table 5. The values in wet state are dominated by water, but ca treatment and the wet-strength additives does mitigate this effect. The sheets not containing a wet-strength additive clearly have the largest loss in out-of-plane modulus. This may be mainly due to a loss in the transverse modulus of the fiber as a result of intrafiber swelling.

We can interpret zero-span measurements, as given in Table 6, as a measure of fiber strength, or, in a less conventional way, as the strength of the network as its density approaches the value of its constituent fibers (18). Surprisingly, for the type of furnish (cotton/linen blend), we do see a significant drop in wet zero-span tensile strength. However, with the exception of the handsheets containing ca treated fibers, the Z_{wet}/Z_{cpd} ratio is close to unity. This result suggests that the drop in wet zero-span tensile strength is due to a loss of interfiber bonding and not a loss in fiber strength. Cowan (19) has shown that zero-span measurements can be affected by interfiber bonding and has proposed that a wet zero-span measurement is a way to minimize this effect. Nevertheless, the ca treatment does emphasize the importance of fiber strength in designing high wet-strength performance papers. In this case, chloroacetic acid improved both dry- and wet-strength bonding levels, but unfortunately degraded fiber strength.

Conclusions

Our attempts to preserve the swollen wet state of paper through critical point drying (cpd) have been reasonably successful.

The retention of wet thickness by critical point drying was higher for the oxidized control and samples with wet-strength additives than for the untreated control, which had the highest degree of swelling.

Bonding index values (n) based on a simple voidal continuum model were determined for the dry, cpd, and wet states of paper. Values for cpd were almost identical with the dry state, while there was a significant reduction in the wet bonding index value. The agreement between the cpd and dry-state bond index values implies that the reduction in strength is mainly attributed to swelling. The loss between the cpd and wet state is ascribed to a reduction in bond strength due to moisture pick up.

Chloroacetic acid treatment appears to be effective in increasing bond strength, but unfortunately this was accomplished with a significant loss in fiber or ultimate network strength.

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Table 1 Basic Sheet Properties at 50% RH

TYPE	GRAMMAGE g/m^2	CALIPER μm	DENSITY g/cm^3	Z.S. Nm/g	E_z/ρ $(k/sec)^2$	Tens. Nm/g
CONTROL	66.4	69.0	0.962	121.9	0.146	56.0
M-F	62.5	80.3	0.778	139.1	0.174	77.8
PAE	63.4	83.3	0.761	131.0	0.173	70.1
PAE/CMC	62.2	78.0	0.797	147.7	0.151	79.6
$ClCH_2COOH$ CONTROL	60.9	104.6	0.582	52.4	0.181	28.9
$ClCH_2COOH$ PAE	60.6	106.1	0.571	65.2	0.191	44.4

Table 2 Wet and CPD Properties $[\theta_{pred} = 1 + (1/\rho_a - 1/\rho_f)]$

TYPE	θ measured	θ predicted	Δθ %	Dry to Wet Thickness Increase %	CPD/WET Thickness Retention %
CONTROL	1.66	1.39	19.4	57.4	86.6
M-F	1.73	1.64	5.48	31.5	94.7
PAE	1.75	1.67	4.79	32.4	95.1
PAE/CMC	1.78	1.61	10.6	30.2	99.8
$ClCH_2COOH$ CONTROL	2.25	2.07	8.70	34.9	98.2
$ClCH_2COOH$ PAE	2.20	2.11	4.37	35.5	91.5

Table 3 Apparent Density and Tensile Ratios

TYPE	ρ_{dry} g/cm^3	ρ_{cpd} g/cm^3	ρ_{wet} g/cm^3	Tcpd/Tdry	Tcpd/Tdry (corrected)	Twet/Tdry
CONTROL	0.962	0.724	0.661	0.531	0.457	0.050
M-F	0.778	0.690	0.571	0.686	0.584	0.349
PAE	0.761	0.673	0.581	0.731	0.640	0.291
PAE/CMC	0.797	0.686	0.597	0.774	0.706	0.322
$ClCH_2COOH$ CONTROL	0.582	0.485	0.452	0.716	0.666	0.092
$ClCH_2COOH$ PAE	0.571	0.529	0.458	0.899	0.849	0.419

Table 4 Bonding Index Values n $[T/T_o = (\rho_a/\rho_f)^{1/n}]$

TYPE	n_{dry}	n_{cpd}	n_{wet}	n_{wet}/n_{cpd}
CONTROL	0.613	0.623	0.238	0.382
M-F	1.19	1.17	0.751	0.642
PAE	1.14	1.12	0.591	0.528
PAE/CMC	1.08	1.52	0.650	0.428
$ClCH_2COOH$ CONTROL	1.65	1.01	0.452	0.448
$ClCH_2COOH$ PAE	2.60	2.48	1.223	0.493

Table 5 Out-of-Plane Longitudinal Specific Modulus Measurements

TYPE	Ez/ρ $(k/sec)^2$ DRY	Ez/ρ^* $(k/sec)^2$ WET	Ez/ρ $(k/sec)^2$ CPD	$(Ez/\rho)_{cpd}/(Ez/\rho)_{dry}$
CONTROL	0.146	0.234	0.035	0.240
M-F	0.174	0.179	0.147	0.845
PAE	0.173	0.204	0.151	0.873
PAE/CMC	0.151	0.174	0.134	0.887
$ClCH_2COOH$ CONTROL	0.181	0.132	0.070	0.387
$ClCH_2COOH$ PAE	0.191	0.196	0.160	0.838

* $(E_z/\rho)_{water} = 0.225\ (k/sec)^2$

Table 6 Zero-span Strength Measurements

TYPE	ZS_{dry} Nm/g	ZS_{cpd} Nm/g	ZS_{wet} Nm/g	ZS_{wet}/ZS_{dry}	ZS_{wet}/ZS_{cpd}
CONTROL	121.9	100.6	101.5	0.833	1.01
M-F	139.1	106.7	102.4	0.736	0.959
PAE	131.0	107.8	107.2	0.818	0.994
PAE/CMC	147.7	105.2	111.5	0.755	1.06
$ClCH_2COOH$ CONTROL	52.4	65.2	40.4	0.772	0.620
$ClCH_2COOH$ PAE	65.2	61.6	50.4	0.773	0.818